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(54) Abstract Title
Aluminium-extruded multi-cavity flat tube having brazing characteristics

(57) An aluminium-extruded multi-cavity flat tube for use in an automotive heat exchanger having excellent brazing characteristics that make it possible to dispense with a flux coating step when assembling a heat exchanger component, or to use an aluminium fin not clad with brazing metals in place of a brazing sheet is provided by pre-coating either a flux composition or a brazing composition on a flat surface of an aluminium-extruded multi-cavity flat tube uniformly with excellent adhesion and transfer print performance. At least one of the flat surfaces of said aluminium-extruded multi-cavity flat tube is coated with a flux composition comprising brazing flux and a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer, or alternatively with brazing composition comprising a brazing flux, brazing metals, and said synthetic resin. In a preferred embodiment, such a coating is provided by applying to a surface of an aluminium-extruded multi-cavity flat tube said compositions as added to an organic solvent, having a molecular structure wherein the atomic ratio of carbon to oxygen is between 2 and 3, through a roll-transfer printing technique.

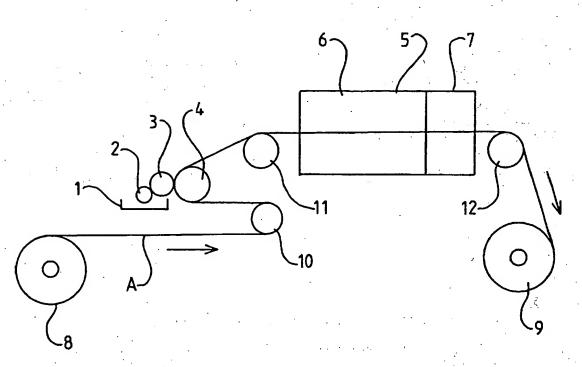


FIG 1

Title:

Aluminium-Extruded Multi-Cavity Flat Tube Having Excellent Brazing Characteristics for use in Automotive Heat Exchanger, and Manufacturing Method Therefor

### **Description of Invention**

The present invention relates to an aluminium-extruded multi-cavity flat tube having excellent brazing characteristics for use in an automotive heat exchanger ("aluminium" herein used includes aluminium alloys). More specifically, the present invention relates to an aluminium-extruded multi-cavity flat tube used for an evaporator, condenser, and the like for use in an automotive air conditioner and a method for manufacturing the same.

Aluminium-made automotive heat exchanger components such as evaporators and condensers for use in automotive air conditioners are manufactured generally from an aluminium-extruded multi-cavity flat tube and a fin that is fabricated into a corrugated shape with a brazing sheet comprising an aluminium core material clad with an A1-Si based brazing metal by assembling them into a prescribed shape and joining them with braze.

In the above application, to destroy and remove aluminium oxides present on the surface of the aluminium-extruded multi-cavity flat tube as well as on the fin and to perform solid brazing, it is necessary to spray-coat the brazing surfaces with a flux suspended either in water or an alcohol after assembling the components into a desired configuration, evaporate the solvent, and thereafter perform the brazing procedure.

However, because of the complex structure of an aluminium-made automotive heat exchanger, it is often difficult to provide the surface of the flat tube or the fin with a uniform coating of the flux suspension, resulting in problems in which solid soldering is hindered at the positions where the flux coating is insufficient or, where the coating is excessive, the flux tends to fall

off within a soldering furnace to contaminate or corrode the furnace, and at the same time spoil the appearance of the processed products.

In recent years, to dispense with the flux coating procedure immediately before the brazing step, a method to coat flux beforehand on the surface of the material to be brazed, a method to coat with a mixed composition of flux and brazing metal, or brazing compositions for such uses have been proposed. (See Japanese Patent Application Laid-Open No. 35870/1991, Japanese Patent application Laid-Open No. 285681/1994, Japanese Patent Publication of the Translation of International Patent Application No. 504485/1994, Japanese Patent No. 2681380, Japanese Patent No. 2681389, and others).

These proposed methods have made it possible to apply a complete coating of flux on the surface of the material to be brazed even with a complex design of the heat exchanger, dispense with the need to use costly brazing sheets in the case where a mixed composition of flux and a brazing metal is applied, and at the same time eliminate the problem of wear on the mould caused by the A1-Si based brazing metal during the fin moulding step because an aluminium plate not clad with a brazing metal can be used.

While the coating step can be performed by a spray method, immersion method, roll-transfer printing, or the like, the spray method has problems such as insufficient coating efficiency or clogging of the spray gun, whereas the immersion method has difficulty in performing a high-speed coating of a composition with a uniform formulation due to precipitation of the brazing metal powders or the flux powders. Accordingly, roll-transfer printing is the most efficient method suitable for a mass manufacturing in actual application.

However, among the organic resins to be evaporated during the heating step for the brazing, when a brazing composition comprising a resin binder such as an acrylic resin that consists of hydrocarbons of the ethylene series is applied with roll-transfer printing, as described in Japanese Patent Application Laid-Open No. 35870/1991, Japanese Patent No. 2681380, and Japanese Patent

No. 2681389, it tends to create many locations where a brazing joint is not completely provided. Furthermore, when a flux composition comprising a surfactant for improving the wettability of the composition on an aluminium material (see Japanese Patent Application Laid-Open No. 285681/1994) is applied with roll-transfer printing, the surfactant acts to hinder the adhesion of the flux composition to cause the impaired brazing characteristics.

A flux composition using an alcohol such as isopropanol as an application medium (see Japanese Patent Publication of the Translation of International Patent Application No. 504485/1994) tends to cause precipitation of the brazing metal powders or the flux powders in the alcohol solution, leading to inferior performance in transfer printing and sometimes causing insufficient adhesion. Therefore, such a composition leaves a problem of inability to attain a solid brazing joint.

The present inventors have conducted extensive experiments and examinations for roll-transfer printing a flux composition or mixed compositions of flux and brazing metals on aluminium materials with a view to solving the above problems. As a result, the inventors have found that transfer printing performance and adhesion of a brazing composition or a flux composition to aluminium materials are significantly influenced by the type of synthetic resins in the composition, properties of organic solvents, and weight ratios of flux or brazing metals to synthetic resins in the compositions.

Based on the above findings, to achieve a continuous, speedy, and efficient coating application of a brazing flux composition and a mixed composition comprising flux and brazing metals on the surface of an aluminium-extruded multi-cavity flat tube used in aluminium automotive heat exchanger components such as evaporators and condensers using a roll-transfer printing technique, the present invention has been achieved as a result of repeated experiments and examinations of diverse nature conducted on

synthetic resins in the composition, organic solvents, weight ratios of flux or brazing metals to synthetic resins in the composition, and their combinations.

Accordingly, an object of the present invention is to provide an aluminium-extruded multi-cavity flat tube for use in automotive heat exchangers, such a tube being prepared with compositions exhibiting satisfactory roll-transfer performance and adhesion and therefore exhibiting excellent brazing characteristics. Furthermore, another object of the present invention is to provide a method for manufacturing an aluminium-extruded multi-cavity flat tube for use in automotive heat exchangers and having the above-described characteristics.

In accordance with the present invention, the aluminium-extruded multi-cavity flat tube for use in automotive heat exchangers to achieve the above objects is characterised by a first feature whereby at least one of the flat surfaces of the tube is coated with a flux composition comprising brazing flux and a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer. The aluminium-extruded multicavity flat tube is further characterised by a second feature whereby such a surface of the tube is coated with a brazing composition comprising a brazing flux, brazing metals, and a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer. The aluminium-extruded multi-cavity flat tube may be further characterised by a third feature whereby the weight ratio of the brazing flux to the synthetic resin in the flux composition, and the weight ratio of the total weight of brazing flux and brazing metals to the synthetic resin in the brazing composition are in the range from 9:1 to 7:3.

In accordance with the present invention, the method for manufacturing an aluminium-extruded multi-cavity flat tube for use in automotive heat exchangers is characterised as follows:-

- 1. At least one of the flat surfaces of an aluminium-extruded multi-cavity flat tube is coated with a mixed flux composition comprising brazing flux powders added to an organic solvent in which a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer is dissolved using a roll-transfer printing technique, and subsequently heated or dried to evaporate the organic solvent in the mixed flux composition.
- 2. At least one of the flat surfaces of an aluminium-extruded multicavity flat tube is coated with a mixed brazing composition comprising brazing flux powders and brazing metal powders added to an organic solvent in which a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer is dissolved using a roll-transfer printing technique, and subsequently heated or dried to evaporate the organic solvent in the mixed brazing composition.
- 3. In the methods of 1 or 2 above, the organic solvent used may be such that the atomic ratio of carbon to oxygen in the molecular structure of said organic solvent is a value between 2 and 3.
- 4. In the methods of 1 or 3 above, the viscosity of the mixed flux composition may be between 100 and 10,000 mPa-s.
- 5. In any one of the methods of 1, 3 and 4 above, the weight ratio of the flux powders to the synthetic resin in the mixed flux composition may be in the range from 9:1 to 7:3.
- 6. In the methods of 2 or 3 above, the viscosity of the mixed brazing composition may be between 100 and 10,000 mPa-s.
- 7. In any one of the methods of 2, 3 and 6 above, the weight ratio of the total of the flux powders and the brazing metal powders to the synthetic resin in the mixed flux composition may be in the range from 9:1 to 7:3.

Figure 1 is a schematic diagram showing one embodiment for a roll-transfer printing a composition onto an aluminium-extruded multi-cavity flat tube.

In the present invention, brazing flux is used to reduce and remove oxide films formed on the surfaces of an aluminium-extruded multi-cavity flat tube, and to facilitate the formation of a eutectic alloy between the aluminium material and the brazing metals. For the above purposes, fluoride-based flux such as KF, AlF<sub>3</sub>, KAlF<sub>4</sub>, K<sub>2</sub>AlF<sub>5</sub>, K<sub>3</sub>AlF<sub>6</sub>, CsF, RbF, LiF, NaF, and CaF<sub>2</sub>, or those that contain the aforementioned compounds as main constituents can be most suitably used. When chloride-based flux is to be used, the residual flux after the brazing procedure must be removed as it could corrode the aluminium material, whereas special handling precautions are required when bromide-based flux is used.

As for the brazing metals, those that form a eutectic alloy with aluminium upon brazing can be used, specific examples for which including Si, Zn, Cu, Ge, and the like. Furthermore, alloys of above metals and aluminium that form a eutectic alloy with aluminium upon brazing can also be used. In an actual application, one or more of the aforementioned metals or alloys can be used.

As for the synthetic resins to be used in the present invention, those mainly comprising a homopolymer of a methacrylate or a copolymer of two or more methacrylates are preferred. Given as specific examples of such a methacrylic acid ester are methyl methacrylate, ethyl methacrylate, propyl methacrylate, 2-methylpropyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, 2-ethylhexyl methacrylate, octyl methacrylate, isodecyl methacrylate, lauryl methacrylate, tridecyl methacrylate, stearyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, diethylaminoethyl methacrylate, 2-hydroxyethyl methacrylate, dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, dimethylaminoethyl methacrylate, t-butylaminoethyl methacrylate, dimethylaminoethyl methacrylate,

methacrylate, and the like. These synthetic resins evaporate at the brazing temperature.

The aluminium-extruded multi-cavity flat tube of the present invention is manufactured by coating at least one of the flat surfaces of the fabricated aluminium-extruded multi-cavity flat tube with a mixed flux composition comprising brazing flux powders added to an organic solvent in which a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer is dissolved, or alternatively with a mixed brazing composition comprising brazing flux powders and brazing metal powders added to the aforementioned organic solvent using a roll-transfer printing technique, and subsequently heating or drying to evaporate the organic solvent comprised in the mixed flux or mixed brazing composition.

It is preferable that the atomic ratio of carbon to oxygen in the molecular structure of the organic solvent to be used for the above purpose be between 2 and 3, and that such a solvent have a certain degree of hydrophilic properties from the viewpoint of transfer printing performance. As the preferable solvent, one or more of the following compounds can be suitably used: 2-propanol, 1-propanol, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol monobutyl ether, propylene glycol monoethyl ether, and the like.

The above flux powders and brazing metal powders to be added to the organic solvent are preferably prepared to a particle diameter of 100µm or less. When the particle diameter exceeds 100µm, the powders in the mixed flux composition or mixed brazing composition tend to precipitate while the compositions are kept in motionless storage, and the uniformity of the suspension deteriorates. In the actual application, it is preferred to use flux powders and brazing metal powders having a particle diameter of 0.1 to 100µm.

The viscosity of the mixed flux composition and mixed brazing composition measured by a cone-late viscometer Mark-E at a revolution speed of 1.0 rpm at 25°C is preferably between 100 and 10,000 mPa-s, and more preferably between 500 and 3,000 mPa-s. If the viscosity is less than 100 mPa-s, the upper side of the compositions coated on the aluminium material becomes rich with the synthetic resin of low specific gravity as the flux powders or brazing metal powders having high specific gravity precipitate during the drying process, causing the brazing characteristics to deteriorate. If the viscosity exceeds 10,000 mPa-s, on the other hand, it makes it difficult to coat the composition evenly and impairs the transfer printing performance. This may lead to a striation of uneven coating thickness generated in the longitudinal direction of the aluminium material, where areas with undersupplied coating provide insufficient contact with the fin and therefore unsatisfactory brazing characteristics.

The weight ratio of the flux powders to the synthetic resin comprised in the mixed flux composition or the weight ratio of the total of the flux powders and the brazing metal powders to the synthetic resin comprised in the mixed flux composition is preferably in the range from 9:1 to 7:3, within which excellent brazing characteristics are obtained. When the weight ratio of the flux powders or the total of the flux powders and the brazing metal powders exceeds 9, adhesion of the respective compositions to the aluminium material becomes insufficient and the coating tends to cause flaking, whereas at less than 7, an excessive ratio of the synthetic resin harms the brazing characteristics and raises the cost.

Roll-transfer printing equipment, for example, has a configuration illustrated in Figure 1, wherein an aluminium-extruded multi-cavity flat tube A supplied from a rewinding unit 8 is sent to a composition application step via a feeder roll 10. In the application step, the composition stored in a composition container 1 is picked up by an attached pick-up roll 2, transferred to an

application roll 3, and then applied to the surface of the aluminium-extruded multi-cavity flat tube A that passes through the application roll 3 and a back-up roll 4.

The aluminium-extruded multi-cavity flat tube A coated with a composition is sent through a feeder roll 11 to a furnace 5 such as a gas furnace that consists of a drying zone 6 and a cooling zone 7. The aluminium-extruded multi-cavity flat tube A, after being heated in the drying zone 6 to a temperature of about 200° to 300°C, is cooled and wound up by a winder unit 9, after passing through a feeder roll 12. While a convection heating system using hot wind is suitable as the heating system for the furnace, radiant heating with far-infrared rays could be jointly used, as well as a supply of air to promote evaporation of organic solvents.

The aluminium-extruded multi-cavity flat tube A passes through the furnace 5 usually within several seconds during which time the organic solvents contained in the composition coated on it evaporate, leaving a coating comprising flux and synthetic resin, or one comprising flux, brazing material, and synthetic resin on one of the flat surfaces of the aluminium-extruded multi-cavity flat tube. While Figure 1 illustrates the equipment configuration for applying a composition on just one side of the flat surfaces of the aluminium-extruded multi-cavity flat tube, both sides of the flat tube can be coated by adding one more composition container and the roll set.

The present invention will be explained in more detail below referring to Examples and Comparative Examples.

### Example 1

As an aluminium material, an 8-cavity extruded flat tube (tube dimensions: 16mm width x 1.8mm thickness, cavity dimensions: 1mm depth x 1.57mm width, with inter-cavity walls of 0.35mm thickness) manufactured by hot extrusions of A1050 material was used. Coatings with compositions of interest were applied to one of the flat surfaces of the above-mentioned

aluminium-extruded multi-cavity flat tube using the equipment shown in Figure 1. The peripheral speed for the application roll (diameter: 30mm), the back-up roll (30mm), and the pick-up roll (12mm) were set at 50 m/min., 50 m/min., and 15 m/min., respectively.

After the coating step, the flat tube was passed through a gas furnace having an ambient temperature of 250°C for 8 seconds to evaporate the organic solvents, cooled, and wound up. In preparing the compositions, all the flux powders and brazing metal powders were sifted through a sieve of 330 mesh (openings/inch), thoroughly mixed and dispersed with a sandmill, and blended and adjusted with organic solvents to a desired viscosity. The viscosity was measured with a cone-plate viscometer Mark-E (manufacturer: Tokimec Inc.) at a speed of 1.0 rpm and at a temperature of 25°C.

Table 1 shows the types of flux, brazing metals, synthetic resins, and organic solvents used as well as the atomic ratios of carbon to oxygen in the molecular structure of the organic solvents. In Table 1, the brazing metal denoted as Si-Zn is a mixture of 90% silicon powder and 10% zinc powder by weight, and Al-Si is a powder of a silicon alloy containing 12% aluminium by weight. Also, the organic solvent denoted as EGMEE is ethylene glycol monoethyl ether, PGMEE is propylene glycol monoethyl ether, DEGMEE is diethylene glycol monobutyl ether, and TEGMEE is triethylene glycol monoethyl ether.

The coating quantity of mixed flux compositions applied was adjusted to  $5 \text{ g/m}^2$  in terms of the flux weight, and the coating quantity of mixed brazing compositions was adjusted to  $5 \text{ g/m}^2$  in terms of the weight of brazing metals contained. Table 2 lists the viscosity, weight ratios of flux to synthetic resins, and weight ratios of combined flux and brazing metals to synthetic resins, respectively, in the compositions used.

Table 1

|          |                                 |          |                           | Organic Solvents |            |
|----------|---------------------------------|----------|---------------------------|------------------|------------|
| Specimen | Flux                            | Brazing  | Synthetic Resin           | Type             | C/O Atomic |
| ID       |                                 | Material | ·                         |                  | Ratio      |
| ,1       | KF-AIF <sub>3</sub>             | . •      |                           | EGMEE            | . 2        |
| 2        | K <sub>3</sub> AlF <sub>6</sub> | -        | Polymer of 2-ethylhexyl   | PGMEE            | 2.5        |
| 3        | KF-AlF <sub>3</sub>             | •        | methacrylate              | 2-Propanol       | 3          |
| 4        | KF-AIF <sub>3</sub>             | -        |                           | DEGMEE           | 2          |
| 5        | KF-AlF <sub>3</sub>             | -        |                           | PGMEE            | 2.5        |
| 6        | K <sub>3</sub> AlF <sub>6</sub> | -        | Copolymer of methyl       | DEGMBE           | 8/3        |
| 7        | KF-AIF <sub>3</sub>             | -        | methacry late and n-butyl | DEGMBE           | 2          |
| 8        | KF-AIF <sub>3</sub>             | -        | methacry late             | 2-Propanol       | 3          |
| 9        | K <sub>2</sub> AlF <sub>5</sub> | -        |                           | DEGMEE           | 2          |
| 10       | KF-AIF <sub>3</sub>             | •.       |                           | PGMEE            | 2.5        |
| 11       | KF-AIF <sub>3</sub>             | Si       | Polymer of 2-ethylhexyl   | 2-Propanol       | . 3        |
| 12       | KF-AlF <sub>3</sub>             | Si-Zn    | methacrylate              | TEGMEE           | 2          |
| 13       | K <sub>2</sub> AlF5             | Si-Zn    | Copolymer of methyl       | 2-Propanol       | 3          |
| 14       | KF-AIF <sub>3</sub>             | Si       | methacrylate and n-butyl  | DEGMEE           | 2          |
| 15       | KF-AIF <sub>3</sub>             | Al-Si    | methacrylate              | DEGMEE           | . 2        |

Table 2

| Specimen ID | Viscosity of composition | Weight ratio of flux and brazing metals to synthetic resin |
|-------------|--------------------------|--|
| ·           | used (mPa-s)             | < (Flux + Brazing metals): Synthetic resin >               |
| 1           | 1,050                    | < (7.5 + 0) : 2.5 >  |
| 2           | 690                      | < (8.0 + 0) : 2.0 >  |
| 3           | 1,890                    | <(8.5+0): 1.5>   |
| 4           | 370                      | < (9.0 + 0) : 1.0 >  |
| . 5         | 710                      | <(7.0 + 0) : 3.0 >   |
| 6           | 2,620                    | < (85+0) 1.5>  |
| 7           | 830                      | < (7.5 + 0) : 2.5 >  |
| 8           | 780                      | <(7.0+0): 3.0>   |
| 9           | 2,290                    | <(8.5 + 0) : 1.5 >   |
| 10          | 120                      | <(7.0 + 0) : 3.0 >   |
| 11          | 8,240                    | <(5.0 + 3.0) : 2.0 >                                       |
| 12          | 3,740                    | <(5.5 + 3.0) : 1.5 >                                       |
| 13          | 9,540                    | <(5.0 + 2.5) : 2.5 >                                       |
| 14          | 2.840                    | <(5.0 + 2.0) : 3.0 >                                       |
| 15          | 1,230                    | <(6.0 + 2.5) : 1.5 >                                       |

The aluminium-extruded multi-cavity flat tubes coated with compositions were evaluated with respect to the adhesive strength and transfer printing performance of the compositions applied. The adhesive strength was evaluated as follows. First, using a thin craft knife, eleven-by-eleven incisions of one-millimetre intervals were made on the coated surface with the depth reaching the aluminium base, to create a grid pattern encompassing one hundred small blocks. 12-mm wide adhesive tape was firmly pressed over the grid pattern and then strongly lifted off in the perpendicular direction, and the number of blocks that stayed un-peeled on the grid was counted.

For the transfer printing performance, evaluation was given in terms of uniformity of the compositions being roll-transferred from the application roll to the aluminium-extruded multi-cavity flat tube, by visually inspecting the condition of the coating. A coating condition that exhibited striations of uneven coating thickness generated in the direction parallel to the extrusion of the flat tube was judged as a failure; otherwise, satisfactory.

Subsequently, a braze joint for evaluation was provided by fitting together an aluminium-extruded multi-cavity flat tube coated with a composition and a fin made of either an aluminium alloy plate (0.1mm in thickness) or an aluminium brazing sheet (core material: A3103 alloy, cladding: A4045 alloy, with a 10% cladding rate) that was moulded into a corrugated shape, heating the assembly up to 600°C in a nitrogen atmosphere, maintaining the temperature for three minutes, and then furnace-cooling the assembly.

The brazing characteristics were evaluated by determining the rate of joining between the aluminium-extruded multi-cavity flat tube and the fin, as expressed in a percentage rate of completed joints per one hundred brazing positions. Table 3 summarises the evaluation results for the adhesive strength and transfer printing performance of the compositions applied, as well as for the brazing characteristics. It can be seen from Table 3 that each of the specimens Nos. 1 through 15 in accordance with the present invention

exhibited 95 or more of un-peeled blocks remaining, formed a uniform coating without striations, and demonstrated excellent brazing characteristics with a rate of joining at 95% or higher.

Table 3

| Specimen ID | Braze joint counterpart | Rate of Joining | Adhesive | Transfer printing |
|-------------|-------------------------|-----------------|----------|-------------------|
|             | Journey purt            | (%)             | strength | performance       |
| 1           | BS                      | 98              | 100      | Satisfactory      |
| 2           | BS                      | 100             | 100      | Satisfactory      |
| 3           | BS                      | 97              | 100      | Satisfactory      |
| 4           | BS                      | 95              | 100      | Satisfactory      |
| 5           | BS                      | 98              | 100      | Satisfactory      |
| 6           | BS                      | 99              | 100      | Satisfactory      |
| 7           | BS                      | 98              | 100      | Satisfactory      |
| <b>8</b> .  | BS                      | 96              | 100      | Satisfactory      |
| 9           | BS                      | 98 ·            | 100      | Satisfactory      |
| 10          | BS                      | 95              | 100      | Satisfactory      |
| 11          | A3003                   | 95              | 100      | Satisfactory      |
| 12          | A3003                   | 100             | 100      | Satisfactory      |
| 13          | A3003                   | 98              | 100      | Satisfactory      |
| 14          | A3003                   | . 99            | 100      | Satisfactory      |
| 15          | A3003                   | 95              | 100      | Satisfactory      |

## Comparative Example 1

Using an aluminium-extruded multi-cavity flat tube identical to Example 1, and also with the identical method as well as conditions, compositions of interest were coated on one of the flat surfaces of the flat tube. After the coating step, similar to Example 1, the flat tube was passed through a gas furnace having an ambient temperature of 250°C for 8 seconds to evaporate off the organic solvents, cooled, and wound up.

Similar to Example 1, the coating quantity of mixed flux compositions was adjusted to  $5 \text{ g/m}^2$  in terms of the flux weight, and that of mixed brazing compositions to  $5 \text{ g/m}^2$  in terms of the weight of brazing metals contained.

Table 4 shows the types of flux, brazing metals, synthetic resins, and organic solvents comprised in the compositions of the Comparative Example 1, as well as the atomic ratios of carbon to oxygen in the molecular structure of the organic solvents used. Table 5 lists the viscosity, weight ratios of flux to synthetic resins, and weight ratios of combined flux and brazing metals to synthetic resins, respectively, in the compositions of the Comparative Example 1 used.

Table 4

|          | • |            | ·  |                  |             |
|----------|---|------------|--|------------------|-------------|
|          |   |            |  | Organic Solvents |             |
| Specimen | Flux                                    | Brazing    | Synthetic Resin                              | Type             | C/O Atomic  |
| ID       | 1 Iu.c                                  | Material   |  |                  | Ratio       |
|          | KF-AlF <sub>3</sub>                     | TVICTORIAL | ,  | EGMEE            | 2           |
| 16<br>17 | K <sub>3</sub> AlF <sub>6</sub>         | _          | Polymer of butyl                             | Ethylbenzene     | 8/0         |
|          | KF-AlF <sub>3</sub>                     | _          | acrylate                                     | PGMEE            | 2.5         |
| 18       |   | _          |  | DEGMEE           | 2           |
| 19       | KF-AIF <sub>3</sub>                     |            | Polymer of                                   | Methyl isobutyl  | 6           |
| 20       | K <sub>2</sub> AlF <sub>5</sub>         | -          | 2-ethylhexyl                                 | ketone           | 2.5         |
| 21       | K <sub>3</sub> AlF <sub>6</sub>         | -          | methacrylate                                 | PGMEE            |             |
| ٠.       | ·                                       |            |  |                  | 8/0         |
| 22 .     | KF-AlF <sub>3</sub>                     |            | Copolymer of methyl                          | Ethylbenzene     | 2           |
| 23       | KF-AlF <sub>3</sub>                     | -          | methacrylate and n-                          | DEGMEE           |             |
| 24       | K <sub>2</sub> AlF <sub>5</sub>         | -          | butyl methacrylate                           | Butanol          | 4           |
| 25       | KF-AIF:                                 | -          |  | Toluene          | 7/0         |
| 26       | KF-AIF                                  | Si-Zn      | Polymer of butyl                             | PGMEE            | 2.5         |
| -27      | KF-AlF <sub>3</sub>                     | Si-Zn      | acrylate                                     | Toluene          | 7/0         |
| 28       | K <sub>2</sub> AlF <sub>3</sub>         | Si         | Copolymer of methyl                          | PGMEE            | 2.5         |
| 1        | KF-AIF <sub>3</sub>                     | Si         | methacry late and n-                         | Cyclohexane      | . 6         |
| 29       | KF-AIF <sub>3</sub>                     | Al-Si      | butyl methacrylate                           | PGMEE            | 2.5         |
| 30       | VL-VIL3                                 | . A1-31    | 1 July 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 |                  | <del></del> |

Table 5

| Specimen ID | Viscosity of composition used (mPa-s) | Weight ratio of flux and brazing metals to synthetic resin |
|-------------|---------------------------------------|--|
| 16          | 850                                   | < (Flux + Brazing metals): Synthetic resin >               |
| 17          | 1,770                                 | <(7.5 + 0) : 2.5 > <(8.0 + 0) : 2.0 >                      |
| 18          | 810                                   | <(6.5 + 0) : 3.5 >   |
| · 19        | 92                                    | <(9.2 + 0) : 8.0 >   |
| 20          | 910                                   | <(8.0+0): 2.0>   |
| 21          | 10,800                                | <(9.2 + 0) : 8:0 >   |
| 22          | 12,400                                | <(9.0+0):1.0>  |
| · · · 23    | 1,480                                 | <(6.0+0): 4.0>   |
| 24          | 3,660                                 | <(8.5+0): 1.5>   |
| 25          | 860                                   | <(7.0+0): 3.0>   |
| 26          | 3,840                                 | <(5.0 + 2.5) : 2.5 >                                       |
| 27          | 4,480                                 | <(6.0 + 2.5) : 1.5 >                                       |
| 28          | 4,730                                 | < (6.2 + 3.0) : 8.0 >                                      |
| 29          | 11,300                                | < (6.0 + 3.0) : 1.0 >                                      |
| 30          | 1,730                                 | <(3.0 + 2.0) : 5.0 >                                       |

The aluminium-extruded multi-cavity flat tubes coated with compositions of the Comparative Example 1 were evaluated for adhesive strength and transfer printing performance using procedures identical to Example 1. Also, the brazing characteristics were evaluated in accordance with procedures identical to Example 1. Table 6 summarises the evaluation results for the above-mentioned experiments. As can be seen from Table 6, the specimens prepared with conditions outside of the restrictions of the present invention exhibited unsatisfactory results in at least one aspect among adhesive strength, transfer printing performance, and brazing characteristics.

Table 6

| Braze joint | Rate of     | Adhesive   | Transfer printing   |
|-------------|-------------|--|---|
| counterpart | Joining     | strength   | performance   |
|             | (%)         |  |   |
| BS          | 85          | 100  | Satisfactory  |
| BS          | 65          | 100  | Failure   |
| BS          | 80          | 100  | Satisfactory  |
| 1           | 95          | 92   | Satisfactory .  |
| 1           | 76          | 100  | Failure   |
|             | 88 .        | 85   | Failure   |
|             | 83          | 100  | Failure   |
|             | 94          | 100  | Satisfactory  |
|             | 75          | 100  | Failure   |
| 1           | 74          | 100  | . Failure   |
| 3           | 55          | 100  | Satisfactory  |
| 1           |             | 100  | Satisfactory.   |
|             |             | 89   | Satisfactory  |
| 1           | 1           | 97   | Failure   |
| 1           | Į.          | 100  | Satisfactory  |
|             | counterpart | Counterpart Joining (%)  BS 85 BS 65 BS 80 BS 95 BS 76 BS 88 BS 83 BS 94 BS 75 BS 75 BS 74 A3003 55 A3003 75 A3003 98 A3003 84 | BS         85         100           BS         65         100           BS         80         100           BS         80         100           BS         95         92           BS         76         100           BS         88         85           BS         83         100           BS         94         100           BS         75         100           BS         74         100           A3003         55         100           A3003         75         100           A3003         98         89           A3003         84         97 |

According to the present invention, either a flux composition or a brazing composition can be uniformly pre-coated on a flat surface of an aluminium-extruded multi-cavity flat tube with excellent adhesion and transfer printing performance, which provides for an aluminium-extruded multi-cavity flat tube for use in an automotive heat exchanger, with excellent brazing characteristics that make it possible to dispense with a flux coating step when assembly a heat exchanger component, or to use an aluminium fin not clad with brazing metals in place of a brazing sheet.

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.

#### CLAIMS

- 1. An aluminium-extruded multi-cavity flat tube having excellent brazing characteristics for use in automotive heat exchangers, wherein at least one of the flat surfaces of the tube is coated with a brazing flux composition comprising brazing flux and a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer.
- 2. An aluminium-extruded multi-cavity flat tube having excellent brazing characteristics for use in automotive heat exchangers, wherein at least one of the flat surfaces is coated with a brazing flux composition comprising a brazing flux, brazing metals, and a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer.
- 3. The aluminium-extruded multi-cavity flat tube according to Claim 1, wherein the weight ratio of the brazing flux to the synthetic resin in the flux composition is in the range from 9:1 to 7:3.
- 4. The aluminium-extruded multi-cavity flat tube according to Claim 2, wherein the weight ratio of a total of brazing flux and brazing metals to the synthetic resin in the brazing composition is in the range from 9:1 to 7:3.
- 5. A method for manufacturing an aluminium-extruded multi-cavity flat tube having excellent brazing characteristics for use in automotive heat exchangers, wherein at least one of the flat surfaces of an aluminium-extruded multi-cavity flat tube is coated with a mixed flux composition comprising brazing flux powders added to an organic solvent in which a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer is dissolved, using a roll-transfer printing technique,

and subsequently heated or dried to evaporate the organic solvent in the mixed flux composition.

- 6. A method for manufacturing an aluminium-extruded multi-cavity flat tube having excellent brazing characteristics for use in automotive heat exchangers, wherein at least one of the flat surfaces of the aluminium-extruded multi-cavity flat tube is coated with a mixed brazing composition comprising brazing flux powders and brazing metal powders added to an organic solvent in which a synthetic resin based, as its main constituent, on a methacrylate homopolymer or a methacrylate copolymer is dissolved, using a roll-transfer printing technique, and subsequently heated or dried to evaporate the organic solvent in the mixed brazing composition.
  - 7. The method according to Claim 5 or Claim 6, wherein the atomic ratio of carbon to oxygen in the molecular structure of said organic solvent is a value between 2 and 3.
  - 8. The method according to Claim 5 or Claim 7, wherein the viscosity of the mixed flux composition is between 100 and 10,000 mPa-s.
  - 9. The method according to any one of Claims 5, 7 and 8, wherein the weight ratio of the flux powders to the synthetic resin comprised within the mixed flux composition is in the range from 9:1 to 7:3.
  - 10. The method according to Claim 6 or Claim 7, wherein the viscosity of the mixed brazing composition is between 100 and 10,000 mPa-s.
  - 11. The method according to any one of Claims 6, 7 and 10, wherein the weight ratio of the total of the flux powders and the brazing metal powders to

the synthetic resin comprised within the mixed flux composition is in the range from 9:1 to 7:3.

- 12. An aluminium-extruded multi-cavity flat tube having excellent brazing characteristics for use in automotive heat exchangers, substantially as hereinbefore described.
- 13. A method for manufacturing an aluminium-extruded multi-cavity flat tube having excellent brazing characteristics for use in automotive heat exchangers, substantially as hereinbefore described.
- 14. Any novel feature or novel combination of features described herein and/or in the accompanying drawings.





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Examiner:

Pete Beddoe

Date of search: 19 Ma

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Int Cl (Ed.6): B23K (35/02, 35/24, 35/28, 35/30, 35/34, 35/36, 35/362, 35/365)

Other: Online: WPI, EPODOC, JAPIO

## Documents considered to be relevant:

| Category | Identity of document and relevant passage   | Relevant<br>to claims |
|----------|---|-----------------------|
| Х        | WO 94/26813 A1 (TEROSON) see esp p15 line 8 - p16 line 11 & exs                       | 1,2,5,6 at least      |
| Х        | US 5690271 (CASTOLIN) see esp exs   | 1,2,5,6 at<br>least   |
| X        | FR 2479055 A & WPI Accession no 81-82045D (SOUDURE) see<br>English abstract           | 1,2,5,6 at<br>least   |
| X        | FR 2193676 A & WPI Accession no 74-03516V (CASTOLIN) see esp exs and English abstract | 1,2,5,6 at<br>least   |
| X,P      | WPI Accession no 99-146884 & JP 11010389 A (HARIMA) 19 January 1999 see abstract      | 1,2,5,6 at<br>least   |

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